Letters to the Editor

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Electronic transition moment variation calculation of coeffieients—A new method

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The study of the variation of electronic transition moment is of importance in the calculations of transition probabilities of bands of diatoms. The expression for the intensity contains an integral $\int \chi_{v'} R_e(r) \chi_{v''} dr$ where $\chi_{v'}$, $\chi_{v''}$ are the vibrational wave functions and Re(r), the electric transition moment. This integral can be solved provided the nature of the function of $R_e(r)$ is known. In the absence of such information, the wave mechanical formulation of the Franck-Condon principle rests on the assumption that the variation of R_e with r is slow and that R_e may be replaced by an average value of $\bar{R}_e$. Then the integral reduces to the form $\bar{R}_e \int \chi_{v'} \chi_{v''} dr$ (Herzberg 1950). Fraser (1954) has shown that R_e is a function of $\bar{r}_{v'v''}$, the mean internuclear distance involved in the particular transition. This provides a means of evaluating $R_e(\bar{r}_{v'v''})$ from the empirical intensities. But R_e is a function of r and hence for more accurate theoretical intensity evaluations, the integral should be evaluated with R_e under the integral (Chamberlain 1961). Assuming $R_e(r)$ variation to be of linear type, $R_e(r) = \text{const}(1+\rho r)$, a method has been suggested by Walvekar (1974) for calculating the coefficient ρ. Assuming $R_e(r)$ variation to be of non-linear type as suggested by Schular (1950), a method is suggested in the present paper for calculating the co-efficient ρ and σ that occur in the expression for $R_e(r) = \text{const}(1+\rho r+\sigma r^2)$. The knowledge of ρ and σ helps to evaluate the theoretical intensities of bands.

The intensity of a band in emission is given by

$$I_{v'v''} = K\gamma^4_{v'v''} N_{v'} [\int \chi_{v'} R_e(r) \chi_{v''} dr]^2, \tag{1}$$

where K is a constant, $N_{v'}$ the population of the level v' and $R_e(r)$ the electronic transition moment. Substituting the value of $R_e(r)$ in the above equation for the non-linear variation as suggested by Schular and re-arranging the equation

following the procedure given by Walvekar (1974) for linear variation of $R_e(r)$ the expressions for ρ and σ are obtained as follows :

$$\rho = \frac{-A - C\sigma}{B}, \qquad \ldots (2)$$

$$\sigma = \frac{\frac{AB'}{B} - A'}{C' - \frac{CB'}{B}}, \qquad \ldots (3)$$

where A, B, C represent the quantities

$$A = \left[\left(\frac{I}{\gamma^4}\right)_2^{\frac{1}{2}} (\int \chi_{v'} \chi_{v''} d_1 r) - \left(\frac{I}{\gamma^4}\right)_1^{\frac{1}{2}} (\int \chi_{v'} \chi_{v''} dr)_2 \right]$$

$$B = \left[\left(\frac{I}{\gamma^4}\right)_2^{\frac{1}{2}} (\int \chi_{v'} r \chi_{v''} dr)_1 - \left(\frac{I}{\gamma^4}\right)_1^{\frac{1}{2}} (\int \chi_{v'} r \chi_{v''} dr)_2 \right]$$

$$C = \left[\left(\frac{I}{\gamma^4}\right)_2^{\frac{1}{2}} (\int \chi_{v'} r^2 \chi_{v''} dr)_1 - \left(\frac{I}{\gamma^4}\right)_1^{\frac{1}{2}} (\int \chi^{v'} r^2 \chi_{v''} dr)_2 \right].$$

The subscripts (1) and (2) are for the bands under consideration in $v''(v' = \text{const})$ progression. Considering two other bands in the same progression, we get similar expressions for A^1, B^1, C^1 where A^1, B^1, C^1, replace A, B, C. The values of A, B, C, and A^1, B^1, C^1, can be obtained by solving the integrals of the type $\int \chi_{v'} \chi_{v''} dr$, $\int \chi_{v'} r \chi_{v''} dr$ and $\int \chi_{v'} r^2 \chi_{v''} dr$ by numerical integration method.

By using the present method calculations have been carried out for Bao $^1\Sigma$–$^1\Sigma$) band system utilizing data already published by the author (1969). Bands (1, 0), (1, 1), and (1, 2) are selected at random for the purpose. The I/γ^4 values and the evaluated values of integrals are reproduced in table 1 below.

Table 1

Band	I/γ^4	$\int \chi_{v'} \chi_{v''} dr$	$\int \chi_{v'} r \chi_{v''} dr$	$\int \chi_{v'} r^2 \chi_{v''} dr$
1, 0	1	0.15194	0.30607	0.617012
1, 1	4.80	0.2700	0.55084	1.12577
1, 2	5.80	0.30679	0.62726	1.2910

Hence the calculated values of (A, B, C), (A^1, B^1, C^1) and (ρ, σ) are as given below :

$A = +0.0522$ $\quad A^1 = -0.0238$ $\quad \rho = -0.3368$

$B = +0.1116$ $\quad B^1 = -0.048$ $\quad \sigma = -0.066597$

$C = +0.22423$ $\quad C^1 = -0.117.$

The equation for $R_e(r)$ reduces to the form

$$R_e(r)' = \text{const}(1-0.3368r-0.066597r^2).$$

Eqs. (2) and (3) help us to calculate the constants ρ and σ, which in turn help help to study the effect of variation of electronic transition moment on the theoretical transition probabilities of bands of the system under consideration.

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X-ray diffraction studies on the thermal expansion of germanium

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A precise knowledge of the thermal expansion of germanium at high temperatures is expected to be of much help for the semiconductor and solid state physicists. Even though many publications have appeared on the thermal expansion of germanium at low temperature paucity of data exists in the high temperature region. For germanium macroscopic thermal expansion measurements have been made by Dennis (1928) from 20-400°C. Nitka (1937) has measured the thermal expansion by X-ray diffraction method and has obtained the average thermal expansion coefficient values to be $6.6\times10^{-6}°C^{-1}$ in the range 20°C to 230°C, $7.3\times10^{-6}°C^{-1}$ in the range 230°C to 450°C and $7.5\times10^{-6}°C^{-1}$ in the range 450°C to 840°C. Straumanis & Aka (1952) have determined the lattice parameters of 99.99% and 99.999% pure germanium in the temperature range 10°C to 50°C and have claimed a great accuracy. The values of the coefficients of thermal expansion as calculated from the lattice parameters reported by them are observed to vary from $5.1\times10^{-6}°C^{-1}$ to $7.44\times10^{-6}°C^{-1}$. Fine (1953) has studied the thermal